JOURNAL OF MATERIALS SCIENCE 25 (1990) 5231–5236

Mechanical properties of zirconia–alumina composite ceramics prepared from Zr–Al metallo-organic compounds

HIDEYUKI YOSHIMATSU*, YOSHINARI MIURA‡, AKIYOSHI OSAKA‡,
HITOSHI KAWASAKI*, SHIGEMI OHMORI*
**Industrial Technology Center of Okayama Prefecture 4-3-18, Ifuku-cho, Okayama-shi, 700 Japan*
‡Faculty of Engineering, Okayama University, 3-1-1, Tsushima Naka, Okayama-shi, 700 Japan

The mixture of a Zr–Al metallo-organic compound and Al_2O_3 powder yields dense ZrO_2–Al_2O_3 composite ceramics. The fraction of the tetragonal ZrO_2 phase in as-sintered ZrO_2–Al_2O_3 ceramics is almost 100% and the ZrO_2 grains at about 500 nm in diameter are dispersed in the matrix. The ceramics have high fracture toughness and bending strength.

1. Introduction

After Claussen [1] indicated that ZrO_2 dispersed Al_2O_3 ceramics have high fracture toughness, Becher [2] reported that the ceramics in which tetragonal ZrO_2 (t-ZrO_2) grains are dispersed have not only high fracture toughness but also high strength. ZrO_2–Al_2O_3 composite powders for the starting materials of such ZrO_2–Al_2O_3 ceramics have been prepared by means of the sol–gel [2], co-precipitation [3] and CVD [4] methods. These methods are the techniques for homogeneous mixing of the compounds of zirconium and aluminium. It has been reported previously [5, 6] that ZrO_2–Al_2O_3composite powders are prepared from some Zr–Al metallo-organic compounds (zircoaluminates) in which zirconium and aluminium atoms are chemically combined by an organofunctional group. ZrO_2 grains of 5 to 200 nm in diameter were homogeneously distributed in the composite particles [7], and the t-ZrO_2 phase in the powders was very stable [5, 6], therefore, the ZrO_2–Al_2O_3 ceramics from zircoaluminate are expected to attain the homogeneous dispersion of t-ZrO_2 and high fracture toughness and strength. It is impossible, however, to change the Zr to Al ratio because commercial zircoaluminates with a fixed Zr to Al ratio are used, although the content of ZrO_2 affects the mechanical properties [1, 2, 4] for the ZrO_2–Al_2O_3 ceramics. Moreover, a preliminary experiment indicated very low sinterability for the powders prepared from the zircoaluminates. In this work, Al_2O_3 powder has been added to the zircoaluminate in order to vary the ZrO_2 content and to improve the stability of the powder. The microstructure and mechanical properties of the ceramics prepared from such powders have been examined.

2. Experimental details

2.1. Preparation of the ZrO_2–Al_2O_3 composite powder

A zircoaluminate compound [8] with $(CH_2)_4COOH$ as the organofunctional group is denoted as ZAC and is supplied by Cavedon Chemical Co., Inc. (Woonsocket, Rhode Island, USA) in the form of about 20% alcohol solution (commercial name: Cavco Mod C). The oxide from ZAC, denoted as ZAC oxide, consists of 16 vol % ZrO_2 and 84 vol % Al_2O_3 (atomic ratio Zr to Al = 0.12). The pure Al_2O_3 powder 100 nm in diameter (commercial name: TM-D) is supplied by Taimei Chemical Industry Co., Ltd. (Nagano Prefecture, Japan).

The Al_2O_3 powder was added to the as-supplied commercial solution of ZAC so as to vary the fraction of the ZAC oxide from 0 to 100 wt %. The mixture was diluted by 3 times with ethyl alcohol and vigorously stirred at 7000 r.p.m. for 0.5 h. The ZAC component in this prepared mixture slurry was turned into gel by dropwise addition of a mixture of 10% NH_4OH aqueous solution and ethyl alcohol followed by rotary-evaporation under a reduced pressure with an aspirator at 50° C. The powder thus obtained was completely dried at 100° C in order to eliminate the alcohol solvent. The dried powder was calcined at a rate of 300° C h^{-1} up to 1100° C in air, held at 1100° C for 2 h, and cooled down in the furnace. The calcined powder was ground for 5 h with an agate ball mill to obtain the ZrO_2–Al_2O_3 composite powder.

The specific surface area of the calcined powders was measured and the morphology of the calcined particles was observed under a scanning electron microscope (SEM).

2.2. Sintering of the ZrO_2–Al_2O_3 ceramics

About 1.2 g of the powder was pressed in a steel die 15 mm in diameter under a pressure of 50 MPa, then pressed isostatically under 200 MPa. The compacts were heated in air at a rate of 300° C h^{-1} up to temperatures between 1500 and 1650° C, held at this temperature for 1 h, and cooled down in the furnace. The compacts in a shape of a rectangular bar about

0022-2461/90 $03.00 + .12

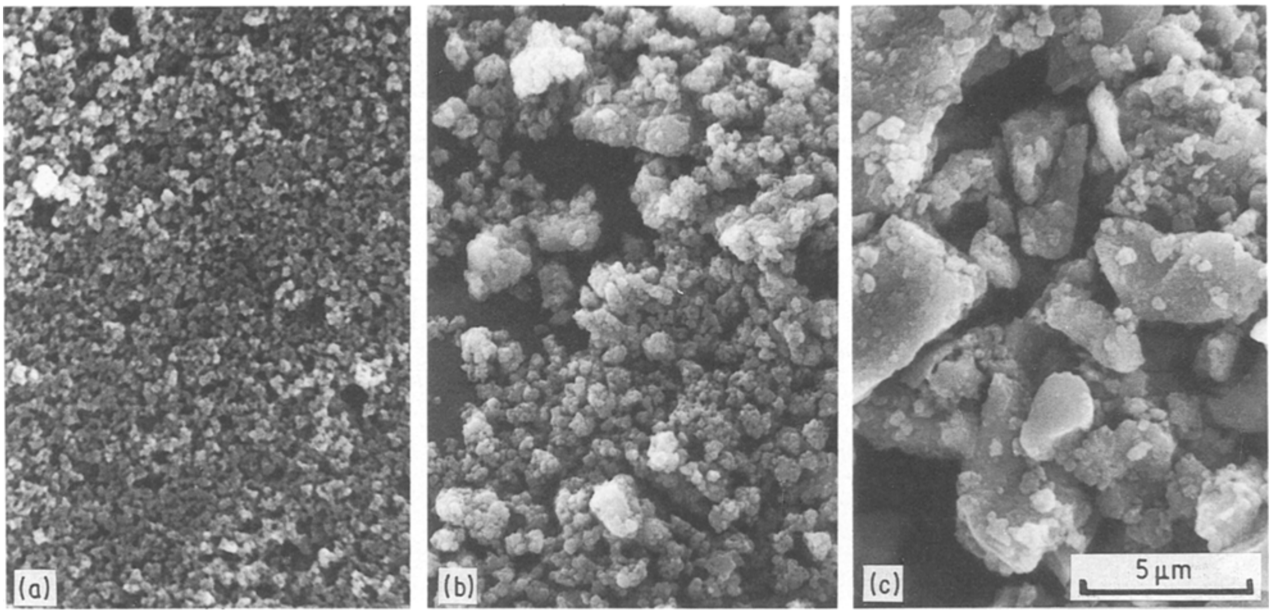

Figure 1 Scanning electron micrographs of ZrO_2–Al_2O_3 composite powders named (a) ZAC50 (8 vol % ZrO_2), (b) ZAC90 (14.4 vol % ZrO_2) and (c) ZAC100 (16 vol % ZrO_2) prepared from the ZAC oxide–Al_2O_3 system, after calcination at 1100° C for 2 h.

$4 \times 3 \times 40\,mm^3$ in size were sintered at 1600° C for 1 h in air. These sintered ceramics were polished with diamond spray 3 µm in diameter, and served for strength determination.

The bulk density for the sintered ceramics was measured by means of the Archimedes' technique. The volume fraction V_t of t-ZrO_2 in the total amount of ZrO_2 for these ceramics was measured by means of the X-ray diffraction technique (CuK_α). V_t was defined as the following equation after Toraya *et al.* [9]

$$X_m = (I_m(1\,1\,\bar{1}) + I_m(1\,1\,1))/(I_t(1\,1\,1) + I_m(1\,1\,\bar{1}) + I_m(1\,1\,1)) \quad (1)$$

$$V_t = (1 - X_m)/(1 + 0.311X_m) \times 100(\%) \quad (2)$$

where the Is denoted the X-ray diffraction intensities corresponding to (1 1 1) and $(1\,1\,\bar{1})$ planes of the t-ZrO_2 and monoclinic ZrO_2 (m-ZrO_2) phases. Since the t-ZrO_2 is the unstable phase at room temperature, parameter V_t represents the stability of the t-ZrO_2 in the ZrO_2–Al_2O_3 ceramics.

The fracture toughness, K_{Ic}, was measured for the polished ceramics with the indentation microfracture (IM) method under 10 kgf load developed by Niihara [10, 11]. K_{Ic} ($MN\,m^{-3/2}$) is defined as [11]

$$(K_{Ic}/Ha^{0.5})(H/E)^{0.4} = 0.018(l/a)^{-0.5} \quad (3)$$

for a Palmqvist crack ($c/a < 2.5$) and

$$K_{Ic}/Ha^{0.5} = 0.203(c/a)^{-1.5} \quad (4)$$

for a Median crack ($c/a \geqslant 2.5$), where a and c denote the distance from the centre to the end of the indent and the front of the crack, respectively; l is calculated by $c - a$; H and E are the hardness and the elastic modulus of the matrix, respectively, for which the reference data of Al_2O_3 (= 370 GPa) [12] is conveniently used. The three-point bending strength was measured with a span of 30 mm at a cross-head speed of $0.5\,mm\,min^{-1}$ in air at room temperature [13].

3. Results

3.1. Morphology of the ZrO_2–Al_2O_3 composite powder

A mixture of x wt % ZAC oxide and $(100 - x)$ wt % added Al_2O_3 will be named ZACx, for example, the mixture of 30 wt % ZAC oxide and 70 wt % Al_2O_3 will be called ZAC30. Accordingly, the powder from ZAC only is represented as ZAC100. Figs 1a, b and c illustrate the SEM photographs for the 1100° C powders of ZAC50, ZAC90 and ZAC100, respectively. It is shown that the particle size decreases with the addition of Al_2O_3 powder. The particles less than 1 µm in diameter are the main constituents of ZAC50. Fig. 2 illustrates the change in the specific surface area (SSA) as a function of the ZrO_2 content for the ZrO_2–

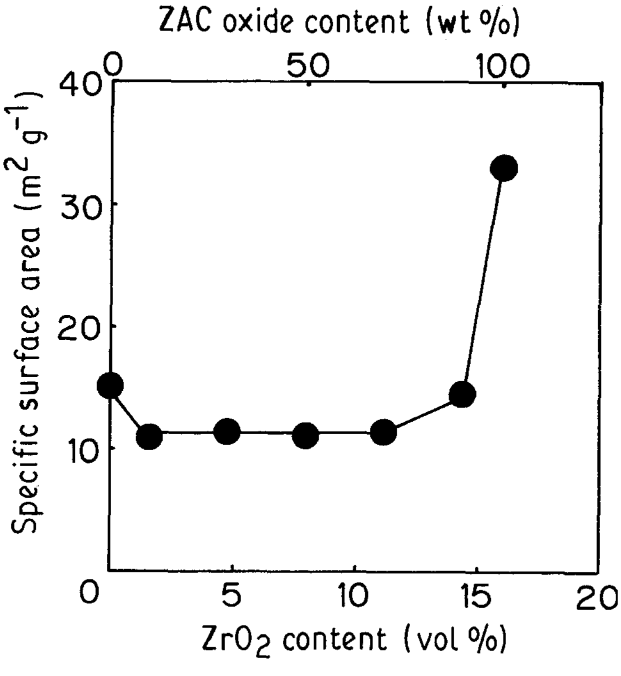

Figure 2 Specific surface area of the ZrO_2–Al_2O_3 composite powders prepared from the ZAC oxide–Al_2O_3 system, after calcination at 1100° C for 2 h.

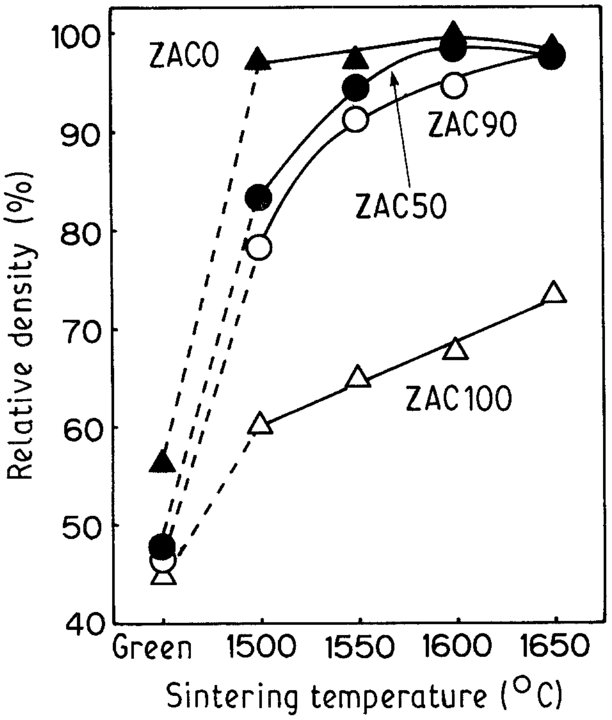

Figure 3 Change in the relative density of the ZrO_2–Al_2O_3 ceramics named ZAC0 (▲) (pure Al_2O_3), ZAC50 (●) (8 vol % ZrO_2), ZAC90 (○) (14.4 vol % ZrO_2) and ZAC100 (△) (16 vol % ZrO_2) with the sintering temperature.

Al_2O_3 powders calcined at 1100° C. The value of SSA is 11 to 15 $m^2 g^{-1}$ for ZAC0 to ZAC90 and is 33 $m^2 g^{-1}$ for ZAC100. The SSA for ZAC100 is higher than that for the other powder, though the particles are bigger for ZAC100 as shown in Fig. 1. It is, therefore, indicated that many pores are present in the particle for ZAC100, but not for ZAC0 to ZAC90.

3.2. Microstructure of ZrO_2–Al_2O_3 ceramics

Fig. 3 illustrates the change in the relative density for ZAC50, ZAC90 and ZAC100 with the sintering temperature, where the density data for ZAC0 (= pure Al_2O_3) are also shown for comparison. ZAC0, ZAC50 and ZAC90 have been densified to 100, 98 and 95%, respectively, due to the sintering at 1600° C for 1 h, while the relative density for ZAC100 is as low as 73% after the sintering even at 1650° C for 1 h. The sinterability for ZAC10, ZAC30 and ZAC70 were approximately as excellent as that for ZAC50. Therefore, Fig. 3 has shown that the addition of Al_2O_3 to ZAC significantly improves the poor sinterability of ZAC100. The fraction of the added Al_2O_3 does not greatly affect the bulk density of the sintered ceramics. Although the reason for the poor sinterability for ZAC100 is not thoroughly understood, it is speculated that the large particles size and specific surface area of the powders, shown in Figs 1 and 2, affect the sinterability for ZAC100. Thus dense (> 95%) ZrO_2–Al_2O_3 ceramics can be prepared from the mixture of the zircoaluminate and Al_2O_3 powder through normal-sintering at 1600° C for 1 h in air.

Figs 4a, b and c are SEM photographs of polished surface for ZAC50, ZAC90 and ZAC100 ceramics, respectively, after sintering at 1600° C for 1 h. Only a small number of pores were observed for ZAC50 and ZAC90, while the porous surface was observed for ZAC100. The ZrO_2 grains about 500 nm in diameter, observed as brighter spots, were homogeneously dispersed in the matrix. Figs 5a, b and c illustrate the photographs of the fractured surface for ZAC0, ZAC10 and ZAC50, respectively, after the sintering at 1600° C for 1 h. The fractured grains 3 to 10 μm in diameter were observed for ZAC0, while the fractured grains 1 to 4 μm and 0.5 to 3 μm in diameter were observed for ZAC10 (1.6 vol % ZrO_2) and ZAC50 (8 vol % ZrO_2), respectively. It has been already reported [4, 14] that the dispersion of ZrO_2 depresses Al_2O_3 grain growth in the ZrO_2–Al_2O_3 ceramics. Lange [14] has confirmed this effect for the ZrO_2–Al_2O_3 ceramics containing > 5 vol % ZrO_2. In the present experiments, however, Fig 5b indicates that as a ZrO_2 content as low as 1.6 vol % depresses the Al_2O_3 grain growth. This is due to the highly homogeneous dispersion of finer ZrO_2 grains in the matrix as described by Hori [4].

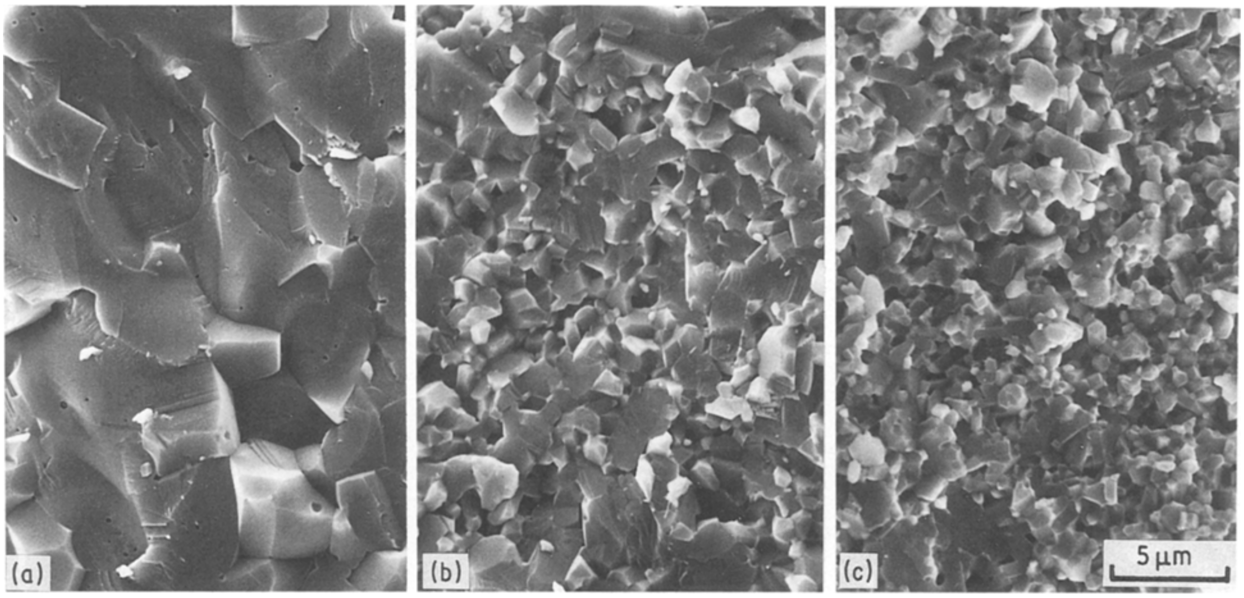

Figure 4 Scanning electron micrographs of the polished surface of ZrO_2–Al_2O_3 ceramics (a) ZAC50 (8 vol % ZrO_2), (b) ZAC90 (14.4 vol % ZrO_2) and (c) ZAC100 (16 vol % ZrO_2) normal-sintered at 1600° C for 1 h.

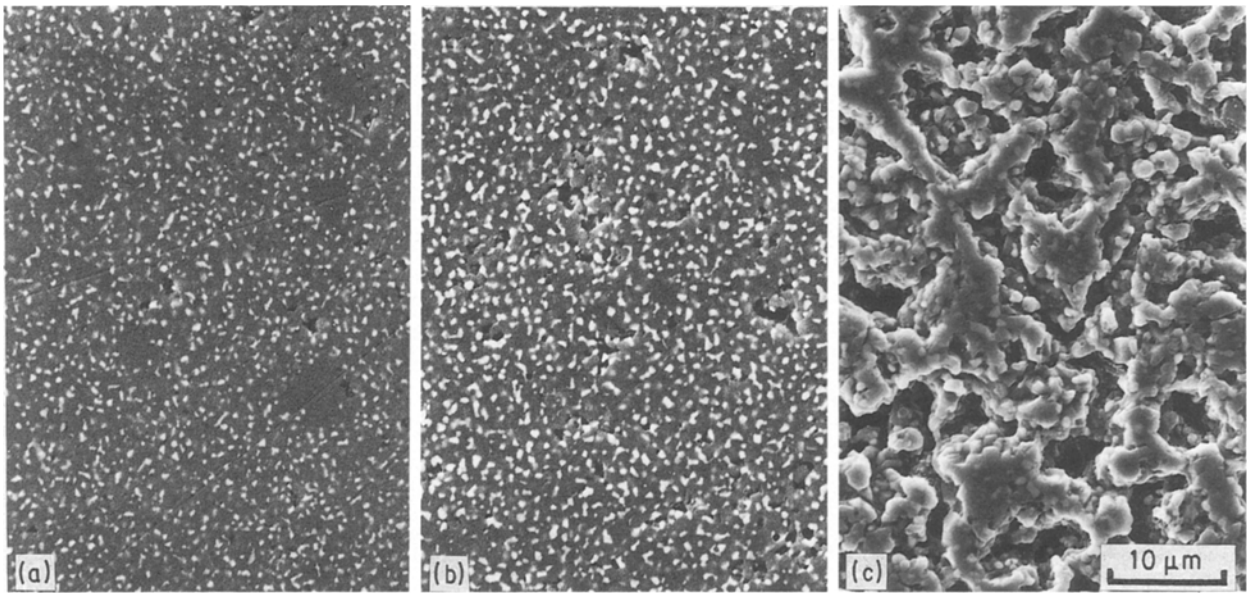

Figure 5 Scanning electron micrographs of the fracture surface of the ZrO_2–Al_2O_3 ceramics (a) ZAC0 (pure Al_2O_3), (b) ZAC10 (1.6 vol % ZrO_2) and (c) ZAC50 (8 vol % ZrO_2) normal-sintered at 1600° C for 1 h.

3.3. Fraction of tetragonal ZrO_2 in ZrO_2–Al_2O_3 ceramics

Fig. 6 illustrates the change in the fraction V_t of t-ZrO_2 of as-sintered surface for ZAC50, ZAC90 and ZAC100 with the sintering temperature. V_t is almost 100% below 1650° C for ZAC50 (8 vol % ZrO_2), and decreases with the increase in the sintering temperature for ZAC90 (14.4 vol % ZrO_2) and ZAC100 (16 vol % ZrO_2). Heuer *et al.* [3] have experimentally shown that t-ZrO_2 grains finer than 600 nm are stable at room temperature. The grain size will increase with both the ZrO_2 content in the ceramics and sintering temperature. This can be confirmed by Fig. 6 showing the dependence of V_t on the ZAC content and sintering temperature. The highest V_t of ZAC50 is therefore attributed to the homogeneous dispersion of the t-ZrO_2 grains finer than 600 nm which size can be evaluated in Fig. 4.

Fig. 7 illustrates V_t of the as-sintered, as-polished and as-fractured surface of the dense ceramics sintered at 1600° C for 1 h as a function of the ZrO_2 content. The data reported by Becher [2], Hori [4] and Lange [15] are also plotted for comparison. Becher's, Hori's and Lange's data are obtained from the hot-pressed specimen (1550 to 1650° C for 15 min to 3 h, as-machined) prepared by sol–gel methods, the normal-sintered one (1550° C for 1 h, as-sintered) prepared by CVD and the hot-pressed specimen (1500° C for 2 h, as-polished) by mixing of ZrO_2 and Al_2O_3 powders, respectively. For the present study, V_t is about 100%

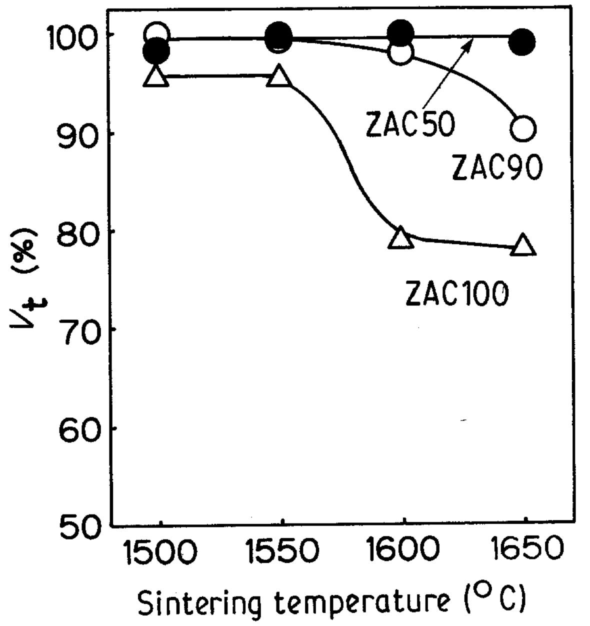

Figure 6 Change in the fraction V_t of tetragonal ZrO_2 of the ZrO_2–Al_2O_3 ceramics named ZAC50 (●) (8 vol % ZrO_2), ZAC90 (○) (14.4 vol % ZrO_2) and ZAC100 (△) (16 vol % ZrO_2) with sintering temperature. For V_t, see text (Equation 2).

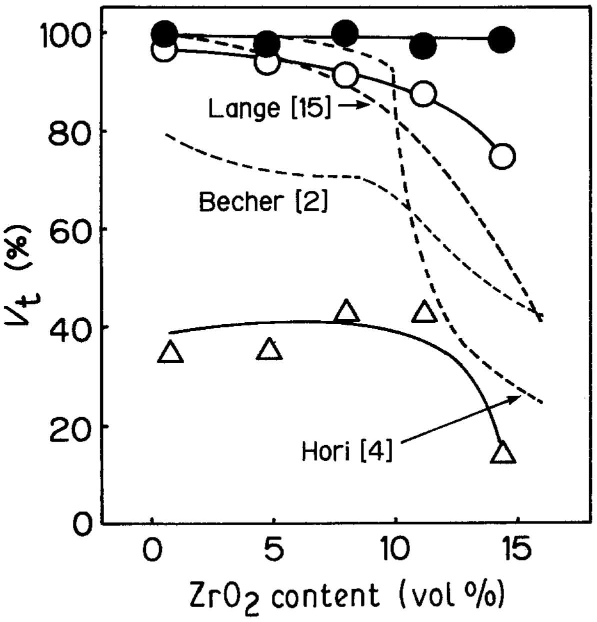

Figure 7 The fraction V_t of tetragonal ZrO_2 of the (●) as-sintered, (○) as-polished and (△) as-fractured surface of ZrO_2–Al_2O_3 ceramics, normal-sintered at 1600° C for 1 h, as a function of ZrO_2 content. The dashed lines indicate the Becher's (as-machined) [2], Hori's (as-sintered) [4] and Lange's (as-polished) [15] data, and for their fabricated condition, see text.

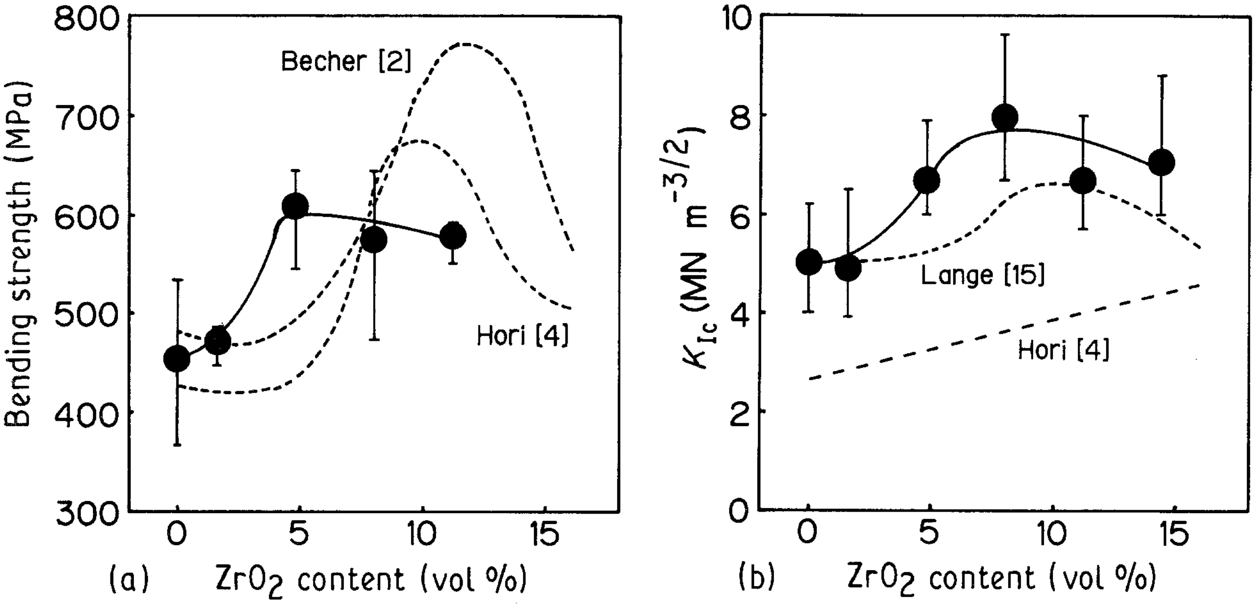

Figure 8 (a) Bending strength of the ZrO_2–Al_2O_3 ceramics normal-sintered at 1600° C for 1 h as a function of ZrO_2 content. Four pieces of specimens are tested for each measurement. The broken lines indicate the Becher's [2] and Hori's [4] data, and for their fabricated condition, see text. (b) Fracture toughness K_{IC} of the ZrO_2–Al_2O_3 ceramics normal-sintered at 1600° C for 1 h as a function of ZrO_2 content. Four pieces of specimens are tested for each measurement. The broken lines indicate the Hori's [4] and Lange's [15] data, and for their fabricated condition, see text.

for as-sintered surface, being independent of the ZrO_2 content. V_t decreased with increasing the ZrO_2 content for as-polished surface, whereas it was kept above 85% for the ceramics with 11 vol % > ZrO_2 content. V_t was decreased to the range between 14 and 43% after the fracture. This decrease of V_t is due to the stress-induced transformation of the tetragonal phase to the monoclinic phase caused by cracking. The stress-induced transformation contributes to the increase of the strength and fracture toughness. The increase in the strength and K_{Ic} of ZrO_2–Al_2O_3 ceramics in the present study is thus expected.

3.4. Mechanical properties of ZrO_2–Al_2O_3 ceramics

Figs 8a and b illustrate the bending strength and the fracture toughness K_{Ic}, respectively, as a function of the ZrO_2 content for the polished ceramics after sintering at 1600° C for 1 h. The data reported by Becher [2], Hori [4] and Lange [15] are also plotted for comparison. Their fabricated conditions are mentioned in Section 3.3, but Hori's specimens were polished and annealed at 1350° C for 1 h. The bending strength for ZAC90 (14.4 vol % ZrO_2) could not be measured because the specimen cracked during the polishing. The dispersion of more than 5 vol % ZrO_2 in an Al_2O_3 matrix causes a significant increase in the bending strength and K_{Ic}. Although the K_{Ic} data are fairly scattered, the average value of K_{Ic} reaches a maximum value of 8 MN m$^{-3/2}$ at 8 vol % ZrO_2.

4. Discussion

One set of data of the stability of tetragonal ZrO_2, strength and fracture toughness cannot be compared with data from another study without caution because the differences may be due to the conditions of fabrication and measurement. Thus the profile of the change in their values with ZrO_2 content will be discussed.

Fig. 7 indicates that the values of V_t of the as-sintered and as-polished ceramics in this study are kept at a high level in the range from 1.6 vol % and 14.4 vol % ZrO_2, while those reported by Becher [2], Hori [4] and Lange [15] rapidly decreased in the range > 8 to 10 vol % ZrO_2 content. The high V_t is related to the dispersion of fine ZrO_2 grains as mentioned in Section 3.3. The dispersed ZrO_2 grains, therefore, remain small in this study even when the ZrO_2 content increases, while the size of the ZrO_2 grains increases in other studies when the ZrO_2 content increases. These effects are caused by using the zircoaluminate for the starting material in this study.

Becher [2] and Hori [4] reported that ceramics with more than 11 vol % ZrO_2 have lower strength because of the dispersion of monoclinic ZrO_2 (lower V_t). Although Hori [4] mentioned that K_{Ic} increased with increasing the fraction of monoclinic ZrO_2 (decreasing V_t), Lange [15] indicated that K_{Ic} decreased with decreasing V_t. On this basis, the dispersion of monoclinic ZrO_2 (= low V_t) may depress the mechanical properties. In this study, the fact that the strength and K_{Ic} of the ceramics in a wide range of compositions from 5 to 14 vol % (11 vol % for strength) ZrO_2 are higher than those the Al_2O_3 ceramics can be attributed to the experimental results that the ZrO_2–Al_2O_3 ceramics maintain the higher levels of V_t.

The strength and K_{Ic} for 5 vol % ZrO_2 in the present study are about 1.3 times as high as that for Al_2O_3 ceramics, while about 7 vol % ZrO_2 needs the same effect in the other experiments [2, 4, 15]. This fact indicates that the dispersion of a lesser amount of ZrO_2 contributes significantly to the improvement of the mechanical properties for ZrO_2–Al_2O_3 ceramics when they are prepared from zircoaluminate. The increase in these parameters is considered to be due both to the depression of Al_2O_3 grain growth and to the higher volume fraction of the tetragonal ZrO_2

phase caused by the homogeneous dispersion of finer ZrO_2 grains in the matrix.

5. Summary

The zircoaluminate ZAC was gelled, dried and calcined under the presence of Al_2O_3 powder to prepare the ZrO_2–Al_2O_3 composite powders. The powders were normal-sintered in air between 1500 and 1650° C for 1 h. The composite powder has finer particles of less than 1 μm in diameter, and lower specific surface area, 11 to 15 $m^2 g^{-1}$, than those of the powder prepared from ZAC only. Although the sinterability is poor for the powder prepared from ZAC only, the addition of Al_2O_3 to ZAC improves the sinterability of ZrO_2–Al_2O_3 powder. The fraction of tetragonal ZrO_2 in the as-sintered specimens is almost 100%, and ZrO_2 grains 500 nm in diameter are homogeneous dispersed in the Al_2O_3 matrix. The bending strength and fracture toughness for the ZrO_2–Al_2O_3 ceramics are higher than those of Al_2O_3 ceramics.

References

1. N. CLAUSSEN, *J. Amer. Ceram. Soc.* **59** (1976) 49.
2. P. F. BECHER, *ibid.* **64** (1981) 37.
3. A. H. HEUER, N. CLAUSSEN, W. M. KRIVEN and M. RÜHLE, *ibid.* **65** (1982) 642.
4. S. HORI, "Two-Component Oxide Ceramics from CVD Powders", Uchida Rokakuhou (Tokyo, Japan, 1988).
5. H. YOSHIMATSU, T. YABUKI and H. KAWASAKI, *J. Non-Cryst. Solids* **100** (1988) 413.
6. H. YOSHIMATSU, H. KAWASAKI and A. OSAKA, *J. Mater. Sci.* **23** (1988) 332.
7. H. YOSHIMATSU, Y. MIURA, A. OSAKA and H. KAWASAKI, *J. Mater. Sci.* **25** (1990) 961.
8. "Technical Catalogue" (Cavedon Chemical Co., Woonsocket, Rhode Island, USA, 1985).
9. H. TORAYA, M. YOSHIMURA and S. SOMIYA, *J. Amer. Ceram. Soc.* **67** (1984) C119.
10. K. NIIHARA, R. MORENA and D. P. H. HASSELMAN, *J. Mater. Sci. Lett.* **1** (1982) 13.
11. K. NIIHARA, *Seramikkusu* (*Bull. Ceram. Soc. Jpn*) **20** (1985) 12.
12. "Fain Ceramics Cyclopedia" (Gihoudou Syuppan, Tokyo, 1987) p. 31.
13. "Testing Method for Flexural Strength (Modulus of Rupture) of High Performance Ceramics", Japan Industrial Standard (JIS) R 1601.
14. F. F. LANGE and M. M. HIRLINGER, *J. Amer. Ceram. Soc.* **67** (1984) 164.
15. F. F. LANGE, *J. Mater. Sci.* **17** (1982) 247.

Received 10 July
and accepted 12 December 1989